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(54) PRODUCTION OF HIGH-PURITY MELAMINE

(57)Abstract:
PURPOSE: To suppress the formation of impurities in a stage of synthesizing melamine and produce the high-purity melamine by heating and reacting urea and/or its thermal decomposition product using a solid acid catalyst having an amount of an acid within a specific range.
CONSTITUTION: This method for producing high-purity melamine is to heat urea and/or its thermal decomposition product at 300-500[deg]C (preferably 350-450[deg]C) reactional temperature in a fluidized bed by using a granular or a powdery solid acid catalyst having 130-400[mu]mol/g amount of an acid measured according to a heat-up eliminating method of NH3 and synthesize the melamine. The average grain diameter of the solid acid catalyst used herein is preferably 10-300[mu]m. Gases in a mixed state produced by the reactional formula or further cyanamide and dicyandiamide coexisting in the reactional system, etc., are cited as the thermal decomposition product of the urea used herein.

CLAIMS

[Claim(s)]
[Claim 1]A urea and/or its pyrolysate to NH3 The manufacture approach of the high grade melamine characterized by compounding a melamine with the reaction temperature of 300-500 degrees C in the fluid bed under existence of the granular or powdery solid acid catalyst which has 130-400micro mol/g of acidity measured by temperature programmed desorption.
[Claim 2]The approach according to claim 1 the mean particle diameter of a solid acid catalyst is 10-300 micrometers.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the manufacture approach of the high grade melamine which uses the solid acid catalyst which has the acidity of the specific range in detail about the manufacture approach of a high grade melamine.
[0002]
[Description of the Prior Art]Generally the melamine is used as raw materials, such as thermosetting resin, a coating, adhesives, and a panel. Mixing of this thermosetting resin, adhesives, and the raw material for panels makes a melamine and formaldehyde react, considers as a methylol-ized melamine, and makes it resinify by carrying out mixing according to each application further. under the present circumstances, reaction time until it resinifies -- a barrack -- it becomes difficult to manufacture a stable product by things. The reaction time of resinification is influenced by the impurity in a melamine, and the fluctuation becomes large, so that there are many impurities. Moreover, in for coatings, if the concentration of the acid impurity in a melamine, AMMERIN, anmelide, cyanuric acid, etc. is high, muddiness is produced and it is not desirable as a raw material melamine. So, there are few impurities and melamine quality with little fluctuation of reaction time is required.
[0003]the DSM method of the low voltage gaseous-phase catalytic reaction which has adopted the wet crystallization method which makes water or an alkali water solution absorb synthesis gas, and it condenses [method] as a process which manufactures a high grade melamine with few impurities, and makes a melamine crystallize. and Chemie Linz -- law etc. is known. However, in the BASF process which makes a melamine crystallize with coolant gas and which has adopted the dry type crystallization method, the purification process which removes the impurity in a melamine is only a gas filter. It is only removing high-boiling point impurities, such as the catalyst particle and MERAMU which come flying from a reactor, and MEREMU, and it is difficult for this to manufacture a high grade article. So, not to mention the process which has adopted the wet crystallization method in a gaseous-phase catalytic-reaction process, in the process which has adopted especially the dry type crystallization method, generation of an impurity is suppressed in a reaction phase and development of the catalyst which compounds a melamine is desired.
[0004]
[Problem(s) to be Solved by the Invention]In compounding a melamine at 300 degrees C - 500 degrees C with the fluid bed under existence of a granular or powdery solid acid catalyst from a urea and/or its pyrolysate, the object of this invention attains development of the catalyst which controls generation of an impurity in the synthetic phase of a melamine, and is to offer the catalyst which manufactures a high grade melamine.

[0005]
[Means for Solving the Problem]this invention persons found out that it was advantageous as a catalyst for which the solid acid catalyst which has the suitable quality of acidity compounds a melamine, as a result of the melamine composition reaction in a low voltage gaseous-phase catalytic-reaction method advancing on an acid catalyst and the quality of acidity inquiring wholeheartedly paying attention to being closely related to a melamine composition reaction that the above-mentioned object should be attained. That is, this invention is a urea and/or its pyrolysate to NH3. It is characterized by compounding a melamine with the reaction temperature of 300 degrees C - 500 degrees C in the fluid bed under existence of the granular or powdery solid acid catalyst which has 130-400micro mol/g of acidity measured by temperature programmed desorption.
[0006]as the class of solid acid catalyst in this invention -- usually -- a commercial scene -- available -- especially -- a limit -- there is nothing -- for example, an activated alumina, a silica, a silica alumina, a zeolite, TiO2, and SnO2 etc. -- metallic oxides and these kinds, or two sorts or more of metal multiple oxides etc. are mentioned.
[0007]This solid acid catalyst is NH3. The acidity measured by temperature programmed desorption is the solid acid catalyst which has 130-400micromol/g, and is 140-300micromol/g preferably. That is, it has the acid site of the strength suitable for a melamine composition reaction, and it is so advantageous to generating a melamine that there are many the amounts. Moreover, although the mechanism is not clear, even if acid strength is too smaller than a proper value and it is too large, it becomes easy to generate an impurity and melamine purity falls. For example, when that whose acid strength is a 100micromol/g grade was used, it was admitted that the compound which has - OH radicals, such as cyanuric acid, as an impurity increased.
[0008]The mean particle diameter of the granular or powdery solid acid catalyst in this invention is 10-300 micrometers in magnitude, and is 30-200 micrometers still more preferably 20-250 micrometers preferably. When this mean particle diameter is smaller than 10 micrometers, a catalyst particle jumps out of a reactor with reactant gas, and it becomes impossible to operate it with industry reactant gas linear velocity as a matter of fact. Moreover, since floating normal irrespective of the configuration of a catalyst particle will no longer be obtained when the relative bulk density to which only a catalyst is applied becomes large if larger than 300 micrometers, it is not desirable.

[0009]Moreover, although especially a convention is not carried out about the particle size distribution of this granular or powdery solid acid catalyst, it is desirable that it is that to which the diameter of grain of maximum size does not exceed 500 micrometers. Moreover, although there is no adverse effect in the reaction itself since pulverized coal 10 micrometers or less flows out out of a reactor with reactant gas even if it is mixing a little, what is necessary is just the amount of extent which does not cause the blinding of the filter of the fines clearance in an after process etc.
[0010]It can change to the gamma-alumina catalyst which has the value with which the acid strength currently used conventionally is not filled this solid acid catalyst into 130micromol/g, or can mix and use. As for the rate in the case of mixing, it is desirable to be unable to specify, especially since it is dependent on the description of the particle of the side mixed, to perform the reaction test in the mixed state actually, and to determine the optimal amount.

[0011]In this invention, although a urea is used as a raw material for compounding a melamine, a urea is a solid-state in ordinary temperature, in the condition of generally having held more than the melting point (132 degrees C), is liquefied and is supplied into a reactor. Since the reactor is usually considerably held from the decomposition temperature (about 160 degrees C) of a urea at the elevated temperature, the supplied urea produces a cyanic acid and ammonia for a pyrolysis according to a lifting and the following type (** 1)

promptly.
[0012]
[Formula 1] (NH2) 2 CO->NCOH+NH3 [0013]The pyrolysate of the urea in this invention is defined including the gas of the mixed state generated by the above-mentioned formula (** 1), a cyanamide, a dicyandiamide which live together in the system of reaction further, etc.
[0014]Generally circulation supply of the gas which removed only the melamine from the outlet gas stream of a reactor as gas for catalyst floating besides an above-mentioned raw material urea is carried out to the reactor of melamine composition at a urea and coincidence.
[0015]The range of the reaction temperature which compounds the melamine in the fluid bed of this invention is 300-500 degrees C, and it is 350-450 degrees C preferably. If reaction temperature does not fulfill 300 degrees C, a reaction rate will fall and the invert ratio to a melamine will fall. Moreover, if 500 degrees C is exceeded, when side reaction other than the main reaction which a melamine generates from isocyanic acid occurs frequently and the melamine by-products, such as an ureido melamine and a cyano melamine, not only increase, but once generated macromolecule-izes, since an impurity like MERAMU or MEREMU increases, it is not desirable.
[0016]
[Example]Hereafter, an example explains this invention still more concretely.

[0017]It is NH3 to a fluidized bed reactor with a bore [example 1 / of 0.3m], and a height of 6m. It was filled up with 150kg (VISTA shrine make and CATAPAL B alumina) of solid acid catalysts of gamma-alumina of the mean particle diameter of 55 micrometers which has 167micro mol/g of acidity measured with the temperature-programmed-desorption measuring device (ATD-700: Ohkurariken make), and 10-300 micrometers of particle size distribution. It is the mixed gas which consists this catalyst of ammonia 75 capacity % and carbon-dioxide-gas 25 capacity % 40Nm/h 3 It leads, and making it fluidize, the melting urea 11kg/h was supplied to the reactor, and reaction temperature made it react by the pressure of 400 degrees C and 0.5-1.0kg/cm2-G. It measured by the approach of showing the invert ratio to the melamine of the urea at this time, and the resinification rate of a product melamine below. Consequently, the invert ratio to a melamine is 77%, and the melamine of the high grade whose resinification rate is 94 minutes was obtained. Moreover, as a result of liquid chromatography's analyzing the cyanuric acid in the melamine at this time, it was 10 ppm or less of limit of detection.
[0018]The invert ratio to the melamine of a urea is expressed with x(amount of generation of melamine) 2.86/ (the supplied amount of ureas). Moreover, a resinification rate is one index of expressing the quality of a melamine, and it is measured as follows. 37wt(s)% formalin 88ml adjusted to pH8.1 is added to product melamine 40g, a resinification reaction is carried out with the constant temperature of 85 degrees C, the 1ml is added into 10ml of 15-degree C distilled water, and the existence of nebula is investigated, and let the shortest reaction time in case nebula is accepted be a resinification rate. Therefore, resinification will be promoted if those impurities of this resinification rate increase in number depending on the amounts of acid impurities contained in a melamine, such as cyanuric acid and AMMERIN. It is supposed that it is the melamine which was excellent in quality with few impurities, so that this resinification rate is slow, and it is used as an index of quality.

[0019]60kg (VISTA shrine make and CATAPAL B alumina) of solid acid catalysts of gamma-alumina of the mean particle diameter of 55 micrometers which has amount mol/g of 167micro of example diacid, and 10-300 micrometers of particle size distribution, and the mean particle diameter of 150 micrometers and 90kg (the product made from CONDEA, CONDEA NW; the conventional catalyst) of synthetic catalysts of gamma-alumina of 45-500 micrometers of particle size distribution which have 114micro mol/g of acidity were mixed, it was filled up with a total of

a 150kg catalyst. and the melamine be compounded on the same conditions as an example 1. For the result, the invert ratio to a melamine was 78%, and the resinification rate was 85 minutes. Moreover, as a result of liquid chromatography's analyzing the cyanuric acid in the melamine at this time, it was 10 ppm or less of limit of detection.

[0020]The reactor was filled up with the mean particle diameter of 150 micrometers and 150kg (the product made from CONDEA, CONDEA NW; the conventional catalyst) of gamma-alumina catalysts of 45-500 micrometers of particle size distribution which have 114micro mol/g of example of comparison 1 acidity, and the melamine was compounded on the same conditions as an example 1. The invert ratio to a melamine is 76%, and the resinification rate was obtained only for the melamine with many impurities by the result in 70 minutes. Moreover, it was 38 ppm as a result of liquid chromatography's analyzing the cyanuric acid in the melamine at this time.

[0021]

[Effect of the Invention]According to this invention, by specifying the acidity of a solid acid catalyst, the approach that the melamine of a high grade can be extremely manufactured compared with the conventional catalyst can be offered, and it is industry top dominance.